

Magnetocaloric effect: A review of the thermodynamic cycles in magnetic refrigeration

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ABSTRACT

Magnetic refrigeration (MR) at room temperature is an emerging technology and shows real potential to enter conventional markets. The principle of MR obeys the magnetocaloric effect (MCE), which is based on the effect caused by a magnetic field on the materials that bear the property of varying the magnetic entropy, as well as its temperature, when varying the magnetic field. This article revises the MCE, its theory and thermodynamics. It discusses the properties that must be met by the magnetocaloric materials as well as those most suitable for room temperature MR and those displaying a promising future. Finally, a presentation and description of the Carnot, Brayton, Ericsson, AMR and cascading MR cycles is given with a view to establishing selection criteria based on their performances.

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1. Introduction

Ozone layer depletion still continues despite measures to protect the ozonosphere in the atmosphere and the ecological environment: the treaty system of ozone layer protection agreed in the Vienna Convention for the Protection of the Ozone Layer

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Nomenclature

ΔT_{ad}	adiabatic temperature change (K)
ΔS_m	isothermal entropy change (J K^{-1})
Δs	specific entropy change ($\text{J kg}^{-1} \text{K}^{-1}$)
T	temperature (K)
H	magnetic intensity (T)
S_T	total entropy (J K^{-1})
S_m	magnetic entropy (J K^{-1})
S_r	lattice entropy (J K^{-1})
S_e	electronic entropy (J K^{-1})
U	internal energy (J)
S	entropy (J K^{-1})
s	specific entropy ($\text{J kg}^{-1} \text{K}^{-1}$)
p	pressure (Pa)
V	volume (m^3)
μ_0	vacuum permeability (N A^{-2})
M	magnetization (A m^{-1})

u	specific internal energy (J kg^{-1})
σ	specific magnetization ($\text{A kg}^{-1} \text{m}^{-1}$)
c	specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
q	heat (J kg^{-1})
T_C	Curie temperature (K)
Q_h	hot source heat (J)
Q_c	cold source heat (J)
T_h	hot source temperature (K)
T_{cold}	cold source temperature (K)

Acronyms

MR	magnetic refrigeration
MCE	magnetocaloric effect
AMR	active magnetic regenerator
ECE	elastocaloric effect

(1985); Montreal Protocol on Substances Depleting the Ozone Layer (1987) and amendments to the Montreal Protocol have provided the schedule to reduce the use of CFCs (chlorofluorocarbons) [1]. On the other hand, the traditional technology of steam compression refrigeration is close to reaching its technical boundaries in achieving further improvements in energy and exergy efficiency, as well as its use of gases with ozone depletion and global warming potential [2]. Therefore, scientists and engineers have begun in recent years to explore new technologies for cooling such as thermoelectric cooling [3], thermoacoustic refrigeration, absorption refrigeration [4,5], adsorption refrigeration [6] and magnetic refrigeration.

Refrigeration systems exploit a material's entropy change due to the variation of an external parameter as well as the pressure or magnetisation to absorb and release energy. Conventional cooling systems (compression based cycles) are based on the elastocaloric effect (ECE). This is defined as the absorption or emission of heat due to the change in pressure on a material (working fluid) in a process where the magnetic field is not applied. Moreover, in the refrigeration technologies based on the MCE, the magnetocaloric effect can be defined as the absorption or emission of heat when a magnetocaloric material is subjected to a change of a magnetic field in a process where the pressure has no influence.

The MCE was first observed by Warburg [7] in 1881, but it was not until 1918 that Weiss and Picard [8] established the physical principles that govern the MCE phenomenon, allowing the first application of the MCE to arise from the proposals of Debye [9] in 1926, and Giauque [10], in 1927, of creating MR cycles in order to reach temperatures below liquid helium. In 1933, Giauque and MacDougall [11] experimentally achieved a temperature value of 250 mK, with paramagnetic salts, overtaking the 1 K barrier for the first time.

The feasibility of MR at room temperature was introduced by Brow in 1976 through a magnetic refrigerator prototype working in accordance with an Ericsson cycle with Gd material and a magnetic field created by superconducting magnets [12]. Pecharsky and Gschneidner's discovery in 1997 [13] of materials with a remarkable magnetocaloric response at room temperature, and the replacement of superconducting magnets with permanent ones in 2001 by the Astronautics Cooperation in USA [14], sparked the interest of scientists, researchers and companies around the world. Since then, numerous publications and patents regarding magnetocaloric materials and magnetic refrigerator

prototypes have been carried out, Yu et al. [15], with most magnetic refrigerator prototypes using a regenerating cycle based on AMR.

In this article, the thermodynamic cycles based on the MCE principle are revised with the aim of establishing selection criteria as on the basis of the expected performance for room temperature refrigeration technology. First, the theory related with the MCE and its associated thermodynamics are described in detail. In the same way, the properties of the magnetocaloric materials needed to fulfil performance requirements, as well as the most suitable materials for MR at room temperature, including those that exhibit a promising future, are described. This article is organised so that in Section 2 the basic theory of MCE and the associated thermodynamics is described. In Section 3, suitable MR materials that fulfil the conditions to be applied as MR as well as their befitting characteristics have been depicted. In Section 4, the available thermodynamic cycles applicable to MR are described. In Section 5, a discussion regarding the practical considerations about MR cycles is carried out. The article ends with appropriated conclusions on the described topics.

2. The MCE theory

The MCE consists of a material's thermal response when subjected to a magnetic field change. It is an intrinsic property of all magnetic materials. It can be quantified as the reversible change in temperature (ΔT_{ad}) in the material when the field change takes place in an adiabatic process, or the reversible change of magnetic entropy (ΔS_m) if the change in field is brought about in an isothermal process. The relationship between the two properties can be illustrated by a schematic diagram T - S (Fig. 1). This diagram represents the thermal dependency of the entropy of a magnetic system depending on the applied field. The existence of MCE at temperature T_0 may cause an adiabatic temperature change in the system $\Delta T_{ad} = T_1 - T_0$ or an isothermal change of magnetic entropy ($\Delta S_m = S_1 - S_2$). The first occurs when the entropy is kept constant, while the second is produced when the temperature is kept constant. Both ΔT_{ad} and ΔS_m are characteristic values of the magnetocaloric effect, according to the initial temperature T_0 and the value of change in the magnetic field. With the increasing value of the external magnetic field change, the ordering of the magnetic spin increases and the magnetic entropy is decreased.

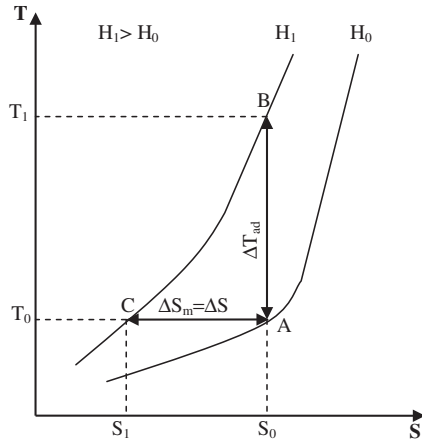


Fig. 1. Thermal dependence of entropy depending on the applied field in a ferromagnetic material.

One of the most important characteristics of a magnetic material is its total entropy (S_T) and the magnetic entropy of the system (S_m). The entropy can be modified by varying the magnetic field, by the temperature and by other thermodynamic parameters. Entropy is a measure of the order in the magneto-thermodynamic system: a high order is related to low entropy and vice versa.

Applying a magnetic field in a ferromagnetic material causes a magnetic ordering of spin of the molecules, orienting themselves in the same direction and lowering the system's entropy. The material's temperature directly influences the kinetics of the electrons and the vibrations of the molecules. Lowering the temperature (releasing energy from the system) promotes a more orderly system and therefore less entropy.

Magnetic entropy (S_m) and its change are closely related to the MCE value and to the magnetic contribution to heat capacity. The magnetic entropy change is also used to determine the characteristics of magnetic refrigerators, such as the capacity of the coolant as well as other characteristics.

The total entropy of a magnetic material can be, according to [16], presented in general at constant pressure as:

$$S_T(H, T) = S_m(H, T) + S_r(T) + S_e(T) \quad (1)$$

where the contribution to the total entropy S_T is given by: magnetic entropy of the magnetisation of the material, lattice entropy caused by the vibrations of crystal lattice and electronic entropy of the material's free electrons (denoted as S_m , S_r , and S_e , respectively) [17]. The lattice and electronic entropy can be considered independent from the magnetic field and only depend on temperature. The magnetic entropy, however, is highly dependent on both the magnetic field and the temperature.

When applying a magnetic field under adiabatic conditions in a ferromagnetic sample (Fig. 2), the total entropy remains constant during the process of magnetisation. Thus, when the magnetic entropy is reduced, lattice and electronic entropy increase to compensate because of the spin lattice connections and vibrations. This causes a temperature increase (ΔT_{ad}) which depends on the applied magnetic field strength. When the external field is removed, the magnetic spin system returns to its original alignment by capturing energy from the lattice, which decreases the thermal entropy and the sample returns to its original temperature.

Individual magnetic moments align with the external field, thereby decreasing the magnetic entropy of the sample and maintaining the S_T . If the magnetic field is removed, the magnetic spin system returns to its original alignment together with the

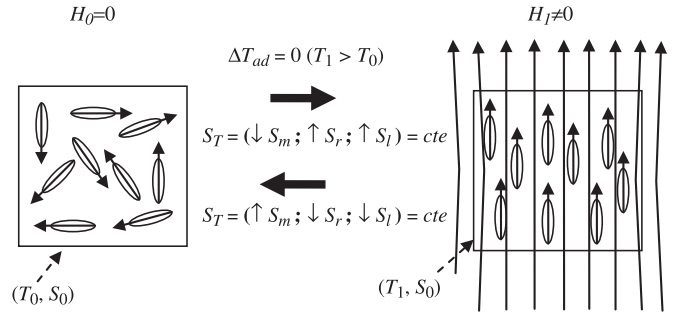


Fig. 2. Arrangement of magnetic spin system of an adiabatic sample before and after applying a magnetic field.

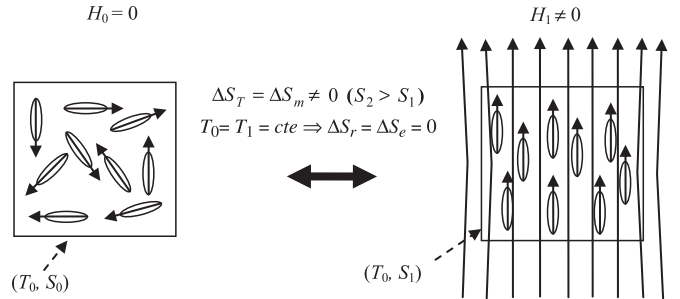


Fig. 3. Arrangement of the magnetic spin system of an isothermal sample before and after applying a magnetic field.

temperature. If the application of magnetic field on the sample is isothermal, the total entropy decreases due to a decrease in the magnetic contribution, since the lattice and electronic entropy do not vary as a result of keeping the temperature constant. This process is schematised in Fig. 3 and shown in Fig. 1.

2.1. Thermodynamics of the MCE

With the joint application of the two Principles of Thermodynamics on a ferromagnetic sample under a magnetic field and considering only the sample as a thermodynamic system, the change in internal energy can be expressed as:

$$dU = TdS - pdV + \mu_0 HdM \quad (2)$$

where H is the intensity of the magnetic field, p the pressure, V is the volume of the sample, μ_0 the magnetic permeability of the vacuum, and M the magnetic momentum of the sample. If the system's volume is not modified, $dV=0$, Eq. (2) is expressed as:

$$dU = TdS + \mu_0 HdM \quad (3)$$

rewriting Eq. (3), which contains extensive magnitudes, depending on specific values per unit mass it follows that:

$$du = Tds + \mu_0 Hd\sigma \quad (4)$$

In this way, σ is defined as the specific magnetisation (magnetic momentum per unit of mass). The total specific entropy change of the system expressed according to H and T can be represented as:

$$ds = (\partial s / \partial T)_H dT + (\partial s / \partial H)_T dH \quad (5)$$

The specific heat c of a substance under a constant state or parameter x can be defined as:

$$c_x = (\delta q / dT)_x \quad (6)$$

When the second law, defined by Eq. (7), is combined with Eq. (6), the specific heat of the substance for an isobaric process

and constant magnetic field (C_{pH}) can be defined as Eq. (8).

$$ds = \delta q/T \quad (7)$$

$$C_{pH} = T(\partial s/\partial T)_H \quad (8)$$

The dependence of the entropy in the magnetic field can be expressed in terms of magnetisation through a Maxwell relation:

$$(\partial s/\partial H)_T = \mu_0(\partial \sigma/\partial T)_H \quad (9)$$

Introducing Eqs. (8) and (9) into Eq. (5), the following expression is obtained for the entropy:

$$ds = (C_{pH}/T)dT + \mu_0(\partial \sigma/\partial T)_H dH \quad (10)$$

The reversible change of temperature (ΔT_{ad}) that the sample undergoes in an adiabatic process of magnetisation (process A–B of Fig. 1) is carried out satisfying Eq. (10) under the condition of $ds=0$, yielding:

$$\Delta T_{ad} = -\mu_0 \int_{H_0}^{H_1} (T/C_{pH})(\partial \sigma/\partial T)_H dH \quad (11)$$

Thus, the MCE sample can be quantified when the field variation takes place in an adiabatic process, according to:

$$MCE_{ad} = -\mu_0 \int_{H_0}^{H_1} (T/C_{pH})(\partial \sigma/\partial T)_H dH \quad (12)$$

It must be taken into account that this equation is not as trivial as it appears as the temperature itself is an implicit function of H given that the temperature will change due to adiabatic temperature change as when altering the magnetic field. This should be included when carrying out integration. The adiabatic temperature change can, of course, also be determined by direct measurements of the sample's temperature.

When the sample is subjected to a variation of the magnetic field in an isothermal process ($dT=0$, process A–C in Fig. 1), the reversible change in entropy ΔS is equal to the magnetic entropy change ΔS_m . The specific entropy change Δs can be determined from Eq. 10, establishing $dT=0$, resulting in the following expression:

$$\Delta s = \Delta s_m = -\mu_0 \int_{H_0}^{H_1} (\partial \sigma/\partial T)_H dH \quad (13)$$

From Eq. (13), the MCE can be quantified if the field variation is performed under an isothermal process.

$$MCE_{isot} = -\mu_0 \int_{H_0}^{H_1} (\partial \sigma/\partial T)_H dH \quad (14)$$

In a process in which the applied field increases ($\Delta H > 0$), the MCE sign is given by the $(\partial \sigma/\partial T)_H$ sign, distinguishing:

- direct MCE, when $(\partial \sigma/\partial T)_H < 0$, resulting $\Delta s_m < 0$ and $\Delta T_{ad} > 0$
- inverse MCE in the opposite case, when $(\partial \sigma/\partial T)_H > 0$, where $\Delta s_m > 0$ and $\Delta T_{ad} < 0$

For most magnetic materials, there is a decrease of magnetisation with temperature and therefore $(\partial \sigma/\partial T)_H$ is negative. So it is seen that $\Delta s_m < 0$ and $\Delta T_{ad} > 0$ for positive field changes.

It can be concluded that the MCE will be large if:

- the magnetic field variation is large
- magnetisation changes rapidly with temperature, i.e., $|(\partial \sigma/\partial T)_H|$ is high.
- the material has a low specific heat.

The change in magnetisation with temperature and specific heat is intrinsic to the material while the change in magnetic field can be controlled externally. In absolute terms, the variation of

magnetisation with temperature $|(\partial \sigma/\partial T)_H|$ is large around the phase transition involving a change of magnetisation in the material.

2.2. First order and second order phase transitions

Transition or phase change is the transformation of a system from one phase to another. The main characteristic is an abrupt change in one or more physical properties. With regard to the phase transition in magnetic systems, two transition modes are given: first order magneto-structural phase transitions and the continuous phase or second order transitions.

2.2.1. First order phase transitions

In first order transitions, there are two phases in equilibrium, so the transformation is not instantaneous and they are linked to the presence of latent heat. They show a discontinuity in the volume, in the magnetisation and entropy, so that $\partial M/\partial T$ and $\partial S/\partial T$ are infinite in the transition temperature. The analysis of the magnetic entropy change and the MCE behaviour in first order magnetic transitions was carried out by Pecharsky et al. [18]. Fig. 4 shows a T – S diagram of a magnetic system experiencing a first order transition with a transition temperature of T_{t0} for a zero field ($H_0=0$) and a transition temperature of T_{t1} for a H_1 ($H_1 > H_0$) field. For each isomagnetic curve of the entropy, depending on the temperature, there is a temperature at which there is an abrupt change in entropy. The vertical lines between the two isomagnetic curves correspond to an adiabatic temperature change (ΔT_{ad}). The adiabatic temperature change achieves its peak values in the scale of temperatures ranging from T_{t0} and T_m (geometrically defined by the dotted lines). For $T_m < T < T_{t0}$, adiabatic temperature changes decrease due to the abrupt change in entropy.

The ferromagnetic materials displaying a first order phase offer an acute magnetocaloric response centred at its transition temperature, rapidly annulling itself in its vicinity [19]. Both are characterised, therefore, by higher values of ΔS_m . There are, however, problems arising from the nature of this phase transition such as [20]:

- existence of thermal and magnetic hysteresis
- changes in volume and thermal stress between the existing phases
- slow kinetic of first order phase transitions that can influence or limit refrigerator performance.

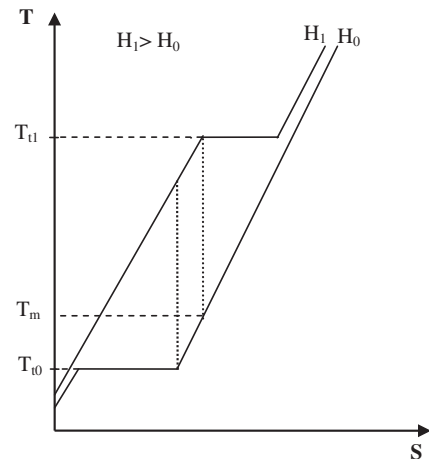


Fig. 4. Schematic T – S diagram of a material in two magnetic fields H_0 and H_1 near the first order transition.

2.2.2. Second order transitions

This type of transition was assumed in order to study the MCE and the entropy changes caused by the magnetic field in Section 2. Second order transitions go continuously from one phase to another without the coexistence of the two in equilibrium. The transformations are verified without discontinuity in the specific values of the volume, magnetisation and entropy and do not exhibit the signs of energy that entropy changes would imply. The second order phase transition is not linked to latent heat. Magnetic transition is the shift from an ordered arrangement of magnetic moments to a disordered arrangement. In materials with this spontaneous magnetisation, the transition temperature is the so-called Curie.

2.3. Influence of temperature on the MCE

The temperature affects the magnetic properties of materials. Increasing the temperature of a solid produces an increase in the magnitude of the atom's thermal vibrations. The atomic magnetic moments can rotate, so that raising the increase in thermal agitation of the atoms tends to misalign the moments. For ferromagnetic materials, both antiferromagnetic and ferromagnetic, atomic thermal movements counteract the coupling strengths between adjacent atomic dipoles, producing some misalignment, irrespective of whether an external field is applied. This produces a decrease in saturation magnetisation for ferromagnetic and antiferromagnetic materials. The saturation magnetisation is highest at 0 K, the temperature at which thermal vibrations are minimal. By increasing the temperature, the saturation magnetisation gradually decreases and then suddenly drops to zero at the so-called Curie temperature (T_C). Hence the T_C can be defined as the lowest temperature at which the magnetisation of a material in the absence of an external field is zero. Above the T_C , the thermal vibrations, i.e., the temperature, is powerful enough to randomise the spins, while below the T_C spontaneous magnetisation occurs. This magnetisation increases with decreasing temperature, due to minor thermal fluctuations. At temperatures above T_C , the ferromagnetic materials become paramagnetic.

Experimentally the T_C can be approximated by the temperature at which the change in magnetisation, $(\partial M/\partial T)_H$, is maximum, which is also where ΔS_m is maximised. In the second order ferro-paramagnetic phase transitions, the MCE will become more intense around T_C . Fig. 5 shows a diagram of the temperature dependence of $(\partial M/\partial T)_H$, ΔS_m and ΔT_{ad} for a variation of field ΔH , giving an overview of the manifestation of the direct MCE in materials exhibiting this type of phase transition. It can be seen that the MCE reaches its peak at around T_C , gently decreasing as we move away from such temperature until it becomes zero. The magnitude of the T_C varies from one material to another depending on its composition.

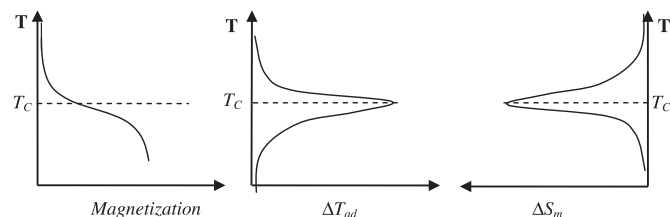


Fig. 5. Thermal dependence of magnetisation and of direct MCE on a material with a 2nd order phase transition for a particular field change ΔH . The MCE is greater in the T_C region.

3. Materials for MR.

All magnetic materials show MCE to a greater or lesser extent. Those which show a higher MCE become potential candidates for MR. However, as pointed out by Yu et al. [21] and Gschneidner et al. [22], the magnetic material must fulfil a series of properties and characteristics in order to be used as cooling material, i.e.,:

- low Debye temperature values
- Curie temperature near working temperature
- large temperature difference (ΔT_{ad}) in the vicinity of phase transition
- no thermal or magnetic hysteresis to enable high operating frequency and, consequently, large cooling power
- low specific heat and high thermal conductivity, thereby allowing large changes in temperature and facilitating the processes of heat transfer and increasing efficiency.
- high electrical resistance in order to avoid Foucault currents in the processes of rapid change in magnetic field.
- non-toxic
- resistant to corrosion
- good mechanical properties
- low manufacturing costs necessary for commercial viability, and
- low environmental impact

Thus, in addition to the magnetic entropy change ΔS_m and ΔT_{ad} , there are a number of other factors to be considered before reaching a coherent decision with regard to the MR material to be used in a commercial magnetic refrigerator.

Materials which exhibit a first order transition reach high values of ΔS_m and ΔT_{ad} . These materials are known as giant magnetocaloric effect materials GMCE [13] and are argued to be the most promising candidates for applications of MR due to their large MCE. However, the problems deriving from the nature of this transition (thermal and magnetic hysteresis, slow kinetic and MCE in a narrow temperature range etc.) can influence or limit the performance of the refrigerators.

An alternative to solid magnetocaloric material to be applied to MR has been proposed by several researchers in theoretical studies using a colloidal suspension of ferromagnetic particles (ferrofluids) [23,24], along with the submission of several patents [25,26]. The technical feasibility of using ferrofluids depends critically on achieving high concentrations of magnetic particles and suitably low yield stress when magnetised, as well as solving heat transfer problems associated with the process. Further research and experimental studies are therefore necessary in order to establish the feasibility of ferrofluids within the scope of MR for practical purposes.

There is currently a wide range of materials that exhibit a significant MCE for a broad spectrum of temperatures. The debate about the different types of materials with their characteristic properties can be found in in-depth studies [27,22]. The majority of the materials are rare earth ones, either pure or combined in alloys, in particular gadolinium compounds.

The research processes of MR to date focus heavily on the study of different types of materials and their properties; ΔS , ΔT_{ad} , related cooling capacity as well as manufacturing costs and feasibility.

3.1. Materials for room temperature MR

In general, room temperature MR uses ferromagnetic materials which possess a high MCE with a Curie temperature approximating room temperature wherein the material undergoes a magnetic phase

transition from an ordered ferromagnetic spin system to a random paramagnetic spin system.

The prototype material for the room temperature range is Gd lanthanide metal, which is ordered ferromagnetically at 294 K. Its magnetocaloric effect has been studied independently by many authors; Benford et al. [28], Ponomarev [29], Tishin et al. [30]. $\Delta T_{ad}/\Delta H$ to T_C values for Gd are approximately 2.8 K/T at low magnetic fields, which drop to approximately 2 K/T in higher magnetic fields.

Among the considerable research on magnetocaloric materials, the majority focus on the search for materials for room temperature, studying their properties and feasibility of being produced economically. Gd–R alloys, where R is another lanthanide metal, (such as Tb, Dy, Ho and Er), were prepared in an attempt to improve Gd in MCE. However, all alloy additions only slightly change the T_C of Gd at lower temperatures without any significant improvement in its MCE. Other candidate materials are: $\text{Fe}_{49}\text{Rh}_{51}$ [31], $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and those related with the $\text{Gd}_5(\text{Si}_{4-x}\text{Ge}_x)$ series [32], the $\text{MnAs}_{1-x}\text{Sb}_x$ [33] series, and the La $(\text{Fe}_{1-x}\text{Co}_x)_{11.9}\text{Si}_{1.1}$ series [34]. The $\text{Fe}_{49}\text{Rh}_{51}$ alloy has a high known MCE value of near room temperature but the high cost of Rh means that it can only be considered for applications researching the cooling capabilities of the materials. The $\text{Gd}_5(\text{Si}_{4-x}\text{Ge}_x)$ and $\text{MnAs}_{1-x}\text{Sb}_x$ series are associated with first order phase transitions, i.e., there are practical obstacles because of the nature of this transition (see above). However, the La $(\text{Fe}_{1-x}\text{Co}_x)_{11.9}\text{Si}_{1.1}$ series is associated with second order phase transitions and its acquirement through powder metallurgical processes allow its production on an industrial scale [35]. The Curie temperature of compounds can be easily adjusted by altering the content of Co. Approximately ΔT_{ad} of 2 K/T can be reached. All this indicates that the compounds of the La $(\text{Fe}_{1-x}\text{Co}_x)_{11.9}\text{Si}_{1.1}$ series can become the room temperature magnetocaloric materials of the future, despite possessing MCE properties inferior to that of Gd metal.

4. MR thermodynamic cycles

In general, a magnetic refrigerator comprises: a magnetic working material, a magnetising/demagnetising system, hot and cold heat exchangers and a heat transfer system with a thermal fluid. The heat transfer fluid is responsible for pumping the heat between the working magnetic material and the hot and cold heat exchangers. Depending on the working temperature, the transfer fluid may be a gas or a liquid. The general working principle of a magnetic refrigerator is as follows: the working material (refrigerant) absorbs heat from the load at a low temperature (the cold heat exchanger) and transfers it to the high temperature source (hot end heat exchanger). As a result of the cyclical repetition of this process, the load is cooled. In magnetic refrigerators the working material is a magnetic material, which changes its temperature and entropy under the effect of a magnetic field. The combination of thermodynamic processes of isothermal magnetisation, (where the refrigerant is magnetised as the temperature is kept constant: during this process the MCE manifests itself as a change in entropy), adiabatic magnetisation (where the coolant temperature increases due to an adiabatic temperature change) and processes at a constant field, allow the achievement of magnetic refrigerators with different thermodynamic cycles.

4.1. Carnot cycle

In MR cycles, the Carnot cycle can be considered as the reference cycle as it allows the direct study of manifestations of the MCE to. The cycle consists of two adiabatic and two

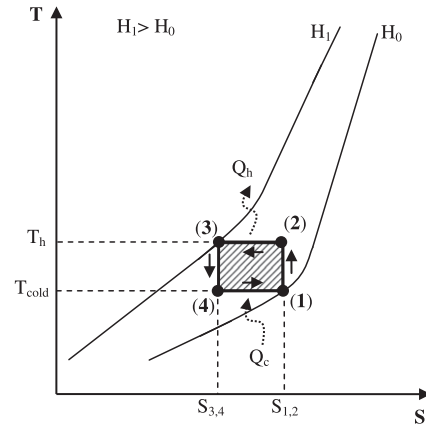


Fig. 6. T–S diagram of an MR Carnot cycle.

isothermal processes and can be illustrated in a T–S diagram between two lines of constant field (Fig. 6).

The magnetic refrigerant is partially magnetised (process 1–2), increasing its temperature adiabatically from T_{cold} to T_h . Then the intensity of the applied magnetic field is increased to complete magnetisation isothermally, making it necessary to remove the refrigerant material's thermal insulation in order to allow the heat exchange with the heat transfer fluid (process 2–3). In this process, the coolant keeps its temperature at constant, while the fluid absorbs the heat generated in the refrigerant due to the magnetisation. In process 3–4, the applied magnetic field decreases and this lowers the temperature of the magnetic refrigerant adiabatically, from T_h to T_{cold} . Finally, the cycle is completed when the material is completely demagnetised during process 4–1. In this process the magnetic refrigerant absorbs heat from the fluid, recovering the energy lost during demagnetisation. To ensure the efficient performance of the system, the fluid rejects the absorbed energy of the magnetised coolant (process 2–3) to the hot source and absorbs energy from the cold source (system to be cooled) that is transferred to the magnetic refrigerant in demagnetising process 4–1.

4.2. Brayton cycle

Heat transfer in the Brayton cycle occurs differently from that of the Carnot cycle. Heat transfer is performed in processes where the magnetic intensity remains constant, thus obtaining higher temperature ranges and consequently a higher heat transfer between the magnetocaloric material and the fluid.

An MR Brayton cycle with regeneration is shown in Fig. 7. The cycle consists of four processes; two adiabatic and two where the intensity of the applied magnetic field remains constant.

Considering the cycle operating processes shown in Fig. 7 from point 1, when the working magnetic material is at temperature T_1 , it undergoes a temperature rise to T_2 (process 1–2) caused by the MCE in the adiabatic magnetisation. Thus the material, in the presence of a constant magnetic field, transfers heat to the hot source (Q_h), lowering its temperature to T_{2a} . The additional cooling of T_{2a} to T_3 is achieved with the aid of the regenerator (process 4_a–1). At point 3, the material undergoes an adiabatic demagnetisation (process 3–4), thus its temperature drops to T_4 . The magnetic material at temperature T_4 exchanges heat (process 4–4_a) with the cold source exchanger (Q_c) absorbing heat so that its temperature increases to T_{4a} . Finally, the regenerator transfers heat to the magnetic material, (process 4_a–1), thereby completing the cycle.

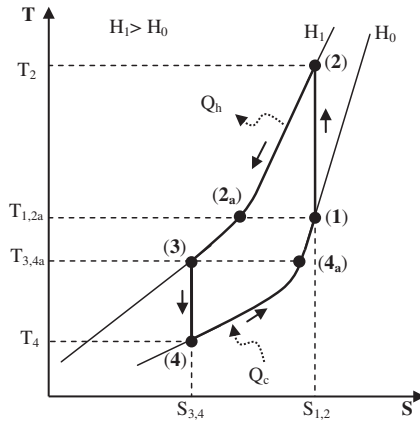


Fig. 7. T - S diagram of an MR Brayton cycle with regeneration.

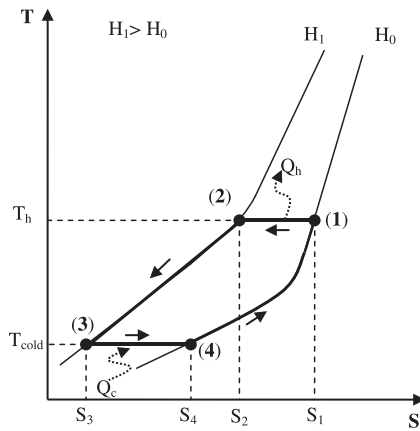


Fig. 8. T - S diagram of an Ericsson cycle with regeneration.

4.3. Ericsson cycle

The Ericsson cycle is a regeneration cycle similar to the Brayton cycle. The only difference is that isothermal magnetisation and demagnetisation is used instead of adiabatic as shown in Fig. 8. In process 1–2 of isothermal magnetisation, the magnetic material rejects heat (Q_h) to the hot source at temperature T_h , and in process 3–4 absorbs (Q_c) from the cold source at temperature T_{cold} . The regeneration corresponds to 2–3 and 4–1 heat exchange processes.

Regeneration, both in the Ericsson cycle as in the Brayton, are only possible with the existence of a difference in temperature that ensures heat transfer. This represents the existence of irreversible processes and, therefore, a decrease in the efficiency of the device.

4.4. Cascade magnetic cycles

Magnetocaloric materials have a temperature at which the MCE is maximum, corresponding to the Curie temperature. As we move away from such temperature, the MCE decreases. In the case of refrigeration processes with high temperature differences, (large span), there is reduced efficiency due to the decrease of MCE because of the deviation of Curie temperature. One solution to this problem is to implement a cascade system of cycles, wherein each cycle has a different material with a Curie temperature in the proximity of its application, so that its working domain and operating temperature range is optimum.

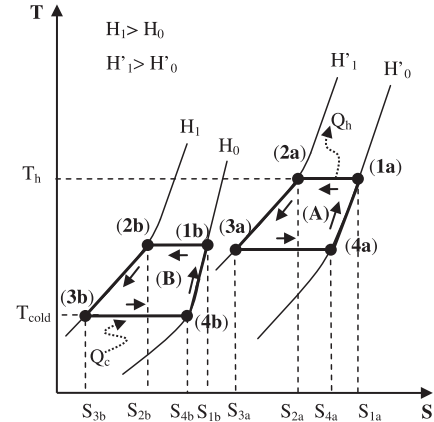


Fig. 9. Magnetic cycle cascade refrigeration cycle based on the Ericsson magnetic cycle.

Fig. 9 displays a cascade process of Ericsson cycles, showing that the cooling power of cycle (A) is used to absorb the energy rejected by cycle (B). The heat absorbed from the cold source by the cascade refrigeration system is represented by the surface S_{4b} , $4b$, $3b$, S_{3b} of cycle (B). The total work carried out in the cascade system is given by the sum of the areas formed by the two cycles, (A) and (B).

A major advantage of an MR cascade system over that of a conventional one is that the MR machine does not require heat exchangers between cycles. This is due to the fact that magnetocaloric material is solid so that the same fluid can be transferred to both cycles.

4.5. Active magnetic regenerator cycle (AMR)

In the AMR cycle, the magnetic material not only serves as a refrigerant providing the temperature change as a result of magnetisation or demagnetisation, but also as a regenerator for the flow of heat transfer. The AMR was introduced in the late seventies by Steyert [36], and subsequently Chen et al. [37] determined that, with the exception of the Carnot cycle, the AMR is the most efficient cycle of MR for room temperature.

The conventional AMR cycle consists of adiabatic magnetisation and demagnetisation and two processes where the intensity of the applied magnetic field remains constant. Due to the nature of the refrigerant (solid), the AMR cycle includes a heat transfer fluid that associates the refrigerant with the cold and hot source heat exchangers. The magnetocaloric regenerator material is immersed into the heat transfer fluid flow and, by means of pistons or pumps, the transfer fluid can move through the regenerator. The AMR cycle cannot be illustrated by a T - S diagram as each part of the regenerator executes single thermodynamic cycles, which bind to one another through the heat transfer fluid.

The operating principle of an AMR refrigerator and its components are illustrated in Fig. 10. The AMR refrigerator comprises: a magnet (1), a regenerator with magnetocaloric material (2), cold (3) and hot source (4) heat exchangers and a device to allow the flow of heat transfer fluid (liquid) through the active regenerator (5). Let us assume that the regenerator is in steady state with the hot and cold source heat exchanger and with a given temperature gradient specified by its temperatures. The AMR cycle experiences four processes represented in Fig. 10: (a) Magnetisation process causing the heating of the magnetocaloric regenerative material, which in turn rejects heat to the heat transfer fluid in the regenerator increasing its temperature, (b) cooling process of the regenerator at constant magnetic field. This process is achieved by the displacement of heat transfer fluid from the regenerator with

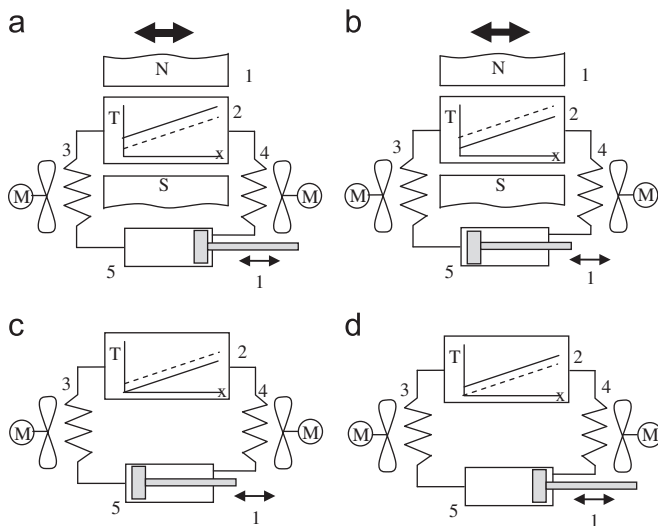


Fig. 10. Schematic illustration of a magnetic refrigerator based on an AMR cycle.

fluid coming from the cold source of the heat exchanger. The fluid absorbs heat from the regenerator and releases it at a higher temperature than that of the hot source in the heat exchanger, (c) demagnetisation process. The regenerator material is cooled by the MCE and absorbs heat from the heat transfer fluid, achieving to lower its temperature below that of the cold source, (d) heating process of the regenerator at constant magnetic field. At zero field the heat transfer fluid, cooled in process (c), is displaced from the regenerator towards the cold source heat exchanger by the fluid from the hot source heat exchanger. The fluid in the cold source heat exchanger absorbs heat, that is, it is the cooling capacity of AMR magnetic refrigerator, thus completing the cycle.

In Fig. 10, the lines inserted into the interior of the regenerator show, by way of example, the temperature profile through the regenerator at a steady state. The dashed line represents the initial profile of the regenerator in each process and the solid line represents the temperature's end profile in that process.

Some authors assume that the AMR cycle can be considered as a group of a series of cascade cycle refrigerators carried out by the active magnetic regenerator material. However, Hall et al. [38] showed that a cascade approach is erroneous. Each solid element does not pump heat from the regenerator directly to the next neighbouring solid element but all elements accept or reject heat to the heat transfer fluid simultaneously and are indirectly coupled through the fluid. This makes the difference between the two cycles clear.

5. Practical considerations for the application of cycles

For practical Carnot cycle based refrigeration, the temperature interval between the hot and cold source is restricted by the adiabatic temperature change of the magnetocaloric material in the processes of magnetisation and demagnetisation. Therefore, the working temperature of the hot and cold source cannot be chosen freely. When the temperature rises, the specific heat and lattice entropy increase, (associated vibrations of atoms), causing the decrease of adiabatic temperature change. When the lattice entropy is very large compared with that of magnetic entropy, the material's adiabatic temperature change is insignificant and requires very large magnetic fields to reduce vibration of the atoms. Furthermore, the Carnot cycle uses a different variable magnetic field in each of the four working points. This requires an electromagnet or a superconducting magnet where the field can

be manipulated, which is inefficient with respect to energy consumption and makes the Carnot cycle unsuitable for normal refrigeration. This limits its application to temperatures below 20 K.

By adding a regenerator to the magnetic refrigeration system, the heat expelled by the lattice system in one stage of the cycle is restored and returned to the lattice system in another stage. Thus the capacity used for system cooling load can be effectively utilised for the increase of effective entropy change and temperature span.

The Brayton and Ericsson cycles are ideal for working with regeneration, in such way that a magnetic refrigerator working temperature span is achieved independently from the working cycle. This enables room temperature MR.

The theoretical Brayton cycle is characterised by the lower cooling capacity and greater heat rejection compared with the theoretical Ericsson cycle. Nevertheless, Cross et al. [39] noted that the differences between the actual Ericsson and Brayton cycles are small due to the deviation of the true isothermal and adiabatic magnetisation in real processes. In [40] an analysis of the second law of Thermodynamics for an ideal Ericsson cycle is carried out.

The AMR are porous to facilitate heat exchange with the transfer fluid and can be formed by thin sheets arranged in parallel, perforated sheets or small spheres of magnetocaloric material [41].

The magnetocaloric material of the regenerator can be a single material or can consist of several with different scaled Curie temperatures. With several materials it is possible to increase the working range of the magnetic refrigerator. This is an apparently intuitive idea. However, issues such as the number of materials used and the relative amount of each are being investigated to achieve optimal performance.

Research groups have developed several prototypes of refrigerators with AMR cycles (see Yu et al. [15]). These can be classified according to: the type of magnetic source (permanent magnets or electromagnets), the type of magnetocaloric material and the relative movement of the active elements of the device. With regard to heat transfer fluid used by the investigators, depending on the temperature range, these can be natural water, glycol water, distilled water, gases (helium) or coolants among others.

6. Conclusions

In this article, both the theory and thermodynamics of the MCE as well as the characteristics and properties required in the magnetocaloric material for magnetic refrigeration have been reviewed. The most suitable materials for room temperature MR as well as those which display a promising future have also been reviewed. A presentation and description is given of the Carnot, Brayton, Ericsson, AMR and cascading MR cycles with a view to establishing selection criteria based on their performances.

The MCE cannot be used directly for cooling; instead specialised cooling cycles with regeneration are required for MR to be used for cooling at room temperature at an effective cost. All described MCE based refrigeration cycles cannot be applied in refrigeration technology at room temperature. In this way, the Carnot cycle can only be effective in cryogenic applications. Nevertheless, the regenerative Brayton and Ericsson cycles are well suited to real applications with little differences between them. The most used MR cycle at room temperature is the AMR cycle due to its greater performance in comparison with the rest of cited cycles. Therefore, all implemented prototypes so far are based on the AMR cycle.

The main refrigerating material used in MR prototypes so far is Gd and its alloys. This is attributed essentially to its good MCE at room temperature, good mechanical properties, low hysteresis, commercial availability and its capacity to meet the needs of engineering. However, its high cost limits its use in large scale applications.

Numerous studies of magnetocaloric materials have been carried out to find alternatives to Gd and are currently the main research field for room temperature MR. Materials with GMCE reach high ΔS_m and ΔT_{ad} values, yet few test devices have been built and studied to determine their performance. These giant MCE materials exhibit problems arising from the nature of their phase transition. In this way, the La (Fe_{1-x}Co_x)_{11.9}Si_{1.1} series could become the room temperature magnetocaloric materials of the future, thanks to their mature industrial scale manufacturing process.

Based on the results of the discussion, it is highlighted that the MR provides an effective alternative to refrigeration based on vapour compression, due to the benefits of using the MCE.

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